CERTIFICATION OF APPROVAL

Fractionation of Crude Oil using Solubility Parameter of Supercritical Carbon Dioxide.

by

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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ABSTRACT

Supercritical fluids (SCF) became one of the significant solvents both for industrial and commercial processes. The reason for that is SCF are neither a liquid nor a gas. SCF have a lower viscosity and higher diffusivity if compared to other liquid solvents which allow SCF to make more effective and faster extraction of solutes. Amongst of all supercritical fluids the supercritical carbon dioxide (SC-CO2) is one of the most important one. The main objective of this paper is to show fractionation of the crude oil into its components not as a traditional distillation method but using supercritical carbon dioxide. Difference of supercritical carbon dioxide fractionation of crude oil is that it uses solubility parameter to fractionate and not the boiling point temperature as it commonly done for the distillation process. By calculating Hildebrand's and Hansen's solubility parameters the best possible extraction conditions will be established.

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INTRODUCTION

1.1 Background

By the extraction of crude oil, I mean the fractionation of the crude oil as an alternative to the distillation. We can use Supercritical Carbon Dioxide to separate the crude oil into components. But the fractionation of the crude oil using supercritical carbon dioxide will be slight different than the products we get from the distillation. Traditional distillation fractionates the component according to their boiling temperatures and thus separation of the components happens at the different stages of the distillatory separator. The larger the molecule the higher the boiling point. And the components the traditional distillation column fractionates are:

- Liquid Petroleum Gas
- Gasoline
- Kerosene
- Diesel
- Lubricating Oil
- Residue

But the fractionation of the crude oil with supercritical carbon dioxide will be based on the solubility of the components. If the solute and the solvent (supercritical carbon dioxide) have the similar solubility parameters then they tend to be miscible. We can make the supercritical carbon dioxide solubility parameter to vary with temperature and pressure, thus enabling the fractionation of the crude oil according to their solubility parameters.

In fractionation of the crude oil with supercritical carbon dioxide we have to notice that the carbon dioxide is non-polar and thus will not be able to separate the non-polar

components. To give some polarity we can dilute the supercritical carbon dioxide with alcohols such as methanol or ethanol.

In the industry this method is not being used, since it is known that the distillation is the cheapest procedure, but again distillation cannot separate isotherms the need of this method may be someday proven to be feasible.

1.2 Problem Statement

In the refinery of the crude oil, distillation column is always consider to be the rule of thumb, it is in mind of every engineer that very first choice for the crude oil fractionation is distillation. Other method only will be considered if the first one is not compatible. But it is important to research the possible alternatives. It is known that the price of carbon dioxide is cheap and its critical temperature is only 31 degrees of Celsius.

And my project is about how much effective can be the fractionation of the crude oil using supercritical carbon dioxide.

1.3 Objective

- To choose the best modeling method for most effective fractionation of crude oil using supercritical carbon dioxide.
- To identify the optimal operating parameters for the maximum solubility in the selective fractionation of the crude oil.

1.4 Scope of Study

- Thermodynamics models uses for the extraction of crude oil. Parameters to be manipulated in the model to achieve best possible mole fraction of the solute in supercritical carbon dioxide.
- Use of model to see the possibility of selective fractionation of crude oil components according to their solubility parameters.

CHAPTER 2
LITERATURE REVIEW AND THEORY

2.1 Supercritical fluids and extraction

If a gas is being compressed to certain pressure it becomes liquid however if the gas was heated beyond particular temperature no amount of pressure will cause it to become liquid. This specific temperature is known as critical temperature and a related vapor pressure to this temperature is known as a critical pressure. The values of critical temperature and critical pressure plot a critical point of the substance. And a state or phase of the fluid which is above its critical point is known as supercritical fluid. In thermodynamics under such conditions there will be no more phase boundaries, meaning there will be only one phase known as supercritical. In the case of a fluid approaching its vapor-liquid critical point liquid and gas phases converge to one phase homogeneous supercritical fluid. For the better understanding the figure of the carbon dioxide pressure vs. temperature phase diagram were put below:

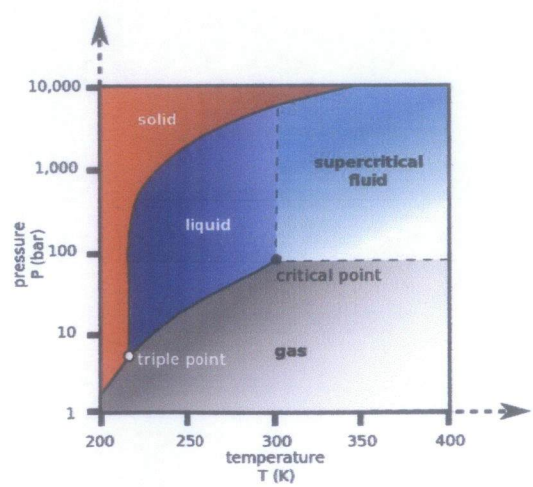


***Figure 1**: carbon dioxide pressure vs. temperature phase diagram*

Very first observation of the supercritical state occurrence was reported in 1822 by Baron Cagniard de la Tour. For the first time in 1879 the solubility of the supercritical fluids on solid were demonstrated. However it is only after 1960 supercritical fluid extraction has experienced a strong expansion.

When the fluid reaches supercritical state it holds many properties of both gas and liquid state. In vicinity of the critical point region it is possible to reach maximum solvent capacity and largest variation of the solvent properties which can be accomplished with only small changes of pressure or temperature. Supercritical fluids offer very favorable extraction properties such as it diffusivity, viscosity, surface tension and other physical properties. Since supercritical fluid is neither gas nor liquid it is diffusivity is higher than of other conventional liquids, which allows rapid mass transfer and faster completion of extraction. More to it has lower viscosity and surface tension than conventional liquid solvents. Supercritical fluid also has the superior dissolving characteristics of a liquid solvent which allows it selective extraction from the complex mixture. But the solvent capacity of supercritical fluid depends on its density, density varies pretty sharp in vicinity of the critical point. Here is table that shows the properties of some supercritical fluids.

Table 1: *Critical Properties of various solvents (Reid et al., 1987)*

Solvent	Molecular weight	Critical temperature	Critical pressure	Critical density
	g/mol	K	MPa (atm)	g/cm^3
Carbon dioxide (CO_2)	44.01	304.1	7.38 (72.8)	0.469
Water (H_2O) (acc. IAPWS)	18.015	647.096	22.064 (217.755)	0.322
Methane (CH_4)	16.04	190.4	4.60 (45.4)	0.162
Ethane (C_2H_6)	30.07	305.3	4.87 (48.1)	0.203
Propane (C_3H_8)	44.09	369.8	4.25 (41.9)	0.217
Ethylene (C_2H_4)	28.05	282.4	5.04 (49.7)	0.215
Propylene (C_3H_6)	42.08	364.9	4.60 (45.4)	0.232
Methanol (CH_3OH)	32.04	512.6	8.09 (79.8)	0.272
Ethanol (C_2H_5OH)	46.07	513.9	6.14 (60.6)	0.276
Acetone (C_3H_6O)	58.08	508.1	4.70 (46.4)	0.278

Advantages of supercritical fluids over liquid phases rest with improved mass transfer processes due to lower fluid viscosities and higher analyte diffusivities, while advantages over gas phases rest with increased molecular interactions due to higher densities (Sairam, Ghosh, Jena, Rao, Banji, 2012).

The most popular of the supercritical fluids is supercritical carbon dioxide. Supercritical carbon dioxide (SC-CO2) is being used as a solvent in variety of the chemical engineering processes, petroleum upgrading and EOR (enhanced oil recovery). SC-CO2 can extract crude oil (hydrocarbon mixture) out of the reservoir and this process is known as EOR (enhanced oil recovery). Also in the chemical processing SC-CO2 extraction is widely popular. It is being used for decaffeination or simply stripping of unwanted materials, extraction of essential oils etc. It can extract solutes both from liquid and solid matrix. Apart from being environmentally non-hazardous and non-toxic carbon dioxide has low critical temperature (30.9 °C) and critical pressure (73.8 bar) which makes SC-CO2 extraction very favorable and popular

There are properties such as solvent density, intermolecular forces between SC-CO2 and crude oil, composition of the crude oil, temperature, pressure and volatility that will have a great impact on the performance of crude oil extraction.

At high enough temperature, no amount of compression can cause liquefaction; that is, the liquid-gas transition is no longer possible. Instead, the substance becomes a supercritical fluid. A supercritical fluid is a fluid that has certain properties of both liquid and gas…. The temperature at which this occurs is called as the critical temperature and the associated pressure is called the critical pressure. The combination of the critical temperature and the critical pressure is called the critical point. (Bottle, Mocerino, Shmid,Wille, *Chemistry, 2008*).

Table below shows the comparison of SC-CO2 and ordinary liquids and gasses.

Table 2: *Physical Properties of Supercritical CO2, Gasses and Liquids.*

Phases	**Density (g/cm2)**	**Viscosity (g/cm.s)**	**Diffusion coefficient (cm2/s)**
Gasses	0.0001-0.0002	0.0001-0.0003	0.1-0.4
Supercritical CO2	0.47	0.0003	0.0007
Liquids	0.6-1.6	0.002-0.03	0.000002-0.00002

Supercritical fluid extraction (SFE) may be defined as separation of chemicals, flavors from the products such as coffee, tea, hops, herbs, and spices which are mixed with supercritical fluid to form a mobile phase. In this process, the mobile phase is subjected to pressures and temperatures near or above the critical point for the purpose of enhancing the mobile phase solvating power (Sairam, Ghosh, Jena, Rao, Banji, 2012).

Supercritical fluid extraction (SFE) has proved to be feasible technically as well as economically for a variety of solid substratum; this fact can be corroborated by the increasing number of industrial SFE units installed worldwide (Melrelez, Zahedi, Hatami , 2008).

One main "advantage" of using SFE is the elimination of organic solvents, thus reducing the problems of their storage and disposal in the lipidologist laboratory. Furthermore, several legislative protocols (such as the EPA Pollution Prevention Act in the USA) have focused on advocating a reduction in the use of organic solvents which could be harmful to the environment. Besides ecological benefits, one of the most interesting properties of SFE is the high diffusion coefficients of lipids in supercritical fluids, far greater than in conventional liquid solvents. Thus, the extraction rates are enhanced and less degradation of solutes occurs. … In addition, carbon dioxide, which is the most adopted supercritical fluid has low cost, is a nonflammable compound and devoid of oxygen... (Sairam, Ghosh, Jena, Rao, Banji, 2012).

2.2 Supercritical carbon dioxide extraction

Supercritical fluid extraction (SFE) of complex hydrocarbon mixtures is important in separation processes, petroleum upgrading and enhanced oil recovery. The performance of a supercritical fluid in fractionating a multicomponent mixture depends on several factors, including the solvent density and differences in volatility and intermolecular forces between the solutes and the supercritical solvent. One of the primary advantages of applications of supercritical fluid extraction or separation is that the fluid density can be varied continuously from gas-like to liquid-like levels by changing the process variables such as pressure and temperature (Hwang, Deo, Vanson, 1996).

The most important of these is the use of the supercritical carbon dioxide as a solvent. Supercritical CO2…Because CO2 is a natural product of biological processes, it is nontoxic, making it well suited for "green chemistry" applications. Supercritical CO2 is currently used as a solvent for dry cleaning, for **petroleum extraction**, for decaffeination and for polymer synthesis (Bottle, Mocerino, Shmid,Wille, *Chemistry, 2008*).

The crude oil interaction with dense carbon dioxide depends predominantly on oil composition, temperature and pressure. The oil recovery improves as pressure rises at increasing density of carbon dioxide achieving maximum at miscibility conditions which occur in liquid–liquid or vapor–liquid–liquid regions. The composition of oil fractions extracted by SC-CO2 varies with pressure. At lower pressures, solvent dilutes more light ends that are in situ upgraded and have a lower density than the initial crude oil and more market value than heavy ends (Rudyk, Hussain, Spirov, 2013).

2.3 Thermodynamic modeling of SC-CO2 extraction and fractionation of crude oil

There are two aspects of modeling the SCF phase equilibrium. One is the prediction of the various critical boundaries such as gas-liquid, liquid-liquid, liquid-liquid-vapor, soli-gas, solid-liquid-gas, etc., in phase diagrams. These predictions are useful in deciding the operating regions where complexities of the phase splitting can be circumvented. The

other aspect is prediction of equilibrium solubility of the solutes in the SCF solvent, their selectivity of separation, and the conditions for optimum recovery and solvent capacity. (Mamata, *Natural Extracts using Supercritical Carbon Dioxide,* 2000)

The accuracy of the solubility prediction is essentially dependent upon the accuracy of the fluid density and fugacity calculation. (Mamata, 2000)

Use of the Peng Robinson cubic equation of state (PR; Peng and Robinson, 1976) is mostly favorable in models for the fugacity calculation where the supercritical fluids are treated like dense gases

$$P = \frac{RT}{V_m - b} - \frac{a\alpha}{V_m^2 + 2bV_m - b^2}$$

Where:

$a = \frac{0.457235\,R^2T_c^2}{P_c}$ $\quad b = \frac{0.077796\,RT_c}{P_c}$ $\quad \alpha = \left(1 + k(1 - T_r^{0.5})\right)^2$

$k = 0.37465 + 1.54226\omega - 0.26992\omega^2$ $\quad \omega = 1.000 - \log_{10}(\frac{P^{sat}}{P_c})_{T_r=0.7}$

V_m- Molar volume

a -accounts for intermolecular interactions between the molecules in the mixture

b-accounts for size difference between molecules of mixture

T_c- Critical temperature $\quad$ R_c-Critical pressure

T_R-Reduced temperature ($T_R = T/T_c$)

When dealing with mixtures, the mixture parameters, a and b, can determined from the quadratic van der Waals mixing rule as:

$$a = \sum_i \sum_j x_i x_j a_{ij}$$

$$a_{ij} = \left(a_{ii} a_{jj}\right)^{0.5} (1.0 - k_{ij})$$

$$b = \sum_i \sum_j x_i x_j b_{ij}$$

$$b_{ij} = 0.5(b_i + b_j)(1.0 - n_{ij})$$

Where k_{ij}, n_{ij} are adjustable binary interaction parameters.

Since in our case we deal with supercritical carbon dioxide extraction of crude oil, we can think of it as vapor-liquid calculation at high pressure.

Regardless of the modeling procedure, the following thermodynamics relationships, or their equivalent relationships in the terms of chemical potential must be satisfied for two phases to be in equilibrium.

$$f_i^V(T, P, y_i) = f_i^L(T, P, x_i), \qquad i = 1,2,3 \ldots m,$$

f_i^L - Fugacity of the components i in the liquid phase.

f_i^V - Fugacity of the component i in the vapor phase.

x_i - Mole fraction of the component i in the liquid phase, and

y_i - Mole fraction of the component i in the vapor or SCF phase.

The most computationally straightforward and thermodynamically consistent method for calculating high-pressure phase behavior is to choose an equation of state to model both the liquid and the vapor or SCF phases. With this approach of fugacity approach the fugacity in each phase can now be written as

$$f_i^L(T, P, x_i) = x_i \varphi_i^L P$$

$$f_i^V(T, P, y_i) = y_i \varphi_i^V P$$

Where φ is fugacity coefficient. (McHugh, Krukonis, *Supercritical Fluid Extractionj, 2nd ed., 1993*).

Fugacity coefficients for the vapor and liquid phases are calculated from the exact thermodynamic relationships. (Prausnitz, 1969)

$$ln\varphi_i^V = \frac{1}{RT}\int_{v^V}^{\infty}\left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_{i\neq j}} - RT\right]dv - ln\left(\frac{Pv^V}{RT}\right)$$

$$ln\varphi_i^L = \frac{1}{RT}\int_{v^L}^{\infty}\left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_{i\neq j}} - RT\right]dv - ln\left(\frac{Pv^L}{RT}\right)$$

Since it is already mentioned earlier before, the fugacity coefficients can be calculated from the Peng-Robinson Equation of State and Van der Waal mixing rules.

$$ln\varphi_i^L = \frac{b_i}{b}\left(\frac{Pv^L}{RT} - 1\right) - \ln\left(\frac{P(v^L - b)}{RT}\right) - \frac{a}{2\sqrt{2}bRT}\left[\frac{2\sum_k x_{ik}a_{ik}}{a} - \frac{b_i}{b}\right] ln\left[\frac{v^L + 2.414b}{v^L + 0.414b}\right]$$

A similar expression can be written for φ_i^V by replacing v^L by v^V and x_i by y_i in the equation (Mamata,2000)

The equation above provided gives us the phase equilibrium between the crude oil and supercritical carbon dioxide. Thus making it possible for us to get the values on the conditions we choose the process to happen.

But not to forget we still need figure out solubility parameters. In the liquids, it is possible to calculate the solubility parameters from the formula:

$$\delta = \left(\Delta\frac{U}{V}\right)^{1/2}$$

$\delta = Solubility\ parameter,\ (cal/cc)^2 = hildebrand$

$U = Internal\ Energy\ change\ during\ vaporization,\qquad (cal/mol)$

$V = Liquid\ molar\ volume, (cc/mol)$

Since in our case we deal with the supercritical condition the formula above will not suit. We will consider supercritical carbon dioxide to be compressed gas. In 1968 and 1969 Giddings and colleagues improved the formula for the solubility parameter formula to

the supercritical fluid solvent by assuming the equality of the liquid solvent and supercritical fluid solvent at a same density with little manipulation for liquid at the boiling temperature. Simply saying Giddings et. Al (1968) proposed "that solvent power of the compressed gas depends on its state relative to its critical condition and its chemical forces" And formula is for solubility parameter for use in supercritical fluid is:

$$\delta = 1.25 P_C^{\frac{1}{2}} (\rho_r / \rho_{r,1})$$

$P_c = critical\ pressure\ of\ the\ gas\ or\ liquid$

$\rho_r = Reduced\ density\ of\ the\ gas\ or\ liquid$

$\rho_{r,1} = Reduced\ density\ of\ the\ gas\ \ or\ liquid\ at\ its\ normal\ boiling\ T \approx 2.66$

Also based on the Hildebrand's regular solution theory of non-polar solute in non-polar solvent we can predict solubility.

$$\ln x_2 = \frac{\Delta H_f}{R}\left(\frac{1}{T_f} - \frac{1}{T}\right) - \frac{V_2 \Phi_1^2 (\delta_2 - \delta_1)^2}{RT}$$

$x_2 = Mole\ fraction\ of\ the\ dissoleved\ solute$

$\Phi_1 = volume\ fraction\ of\ component\ 1$

$\Delta H_f = Heat\ of\ fusion$

$T_f = Melting\ point\ of\ the\ solute$

$T = Temperature\ of\ solution$

By looking at the equitation above it can be easily noticed that the maximum solubility is going to be when solubility parameters (δ_1, δ_2) are equal or very close to each other. It tells us that similar solubility parameters tend to be miscible and that is why we can manipulate supercritical carbon dioxide solubility parameter for selective fractionation of the crude oil component. But we should remember that above equation is only true for non-polar solutions; simply it won't work if it is polar molecules. And always keep in mind that like only dissolves like.

Below I have attached the values of the Hildebrand solubility for some molecule:

Table 3: *Hildebrand Solubility Parameters*

Standard Hildebrand values from Hansen. Journal of Paint TechnologyVol. 39, No. 505, Feb 1967

Sl Hildebrand values from Barton.Handbook of Solubility Parameters, CRC Press, 1983

Values in parenthesis from Crowley. et al., Journal of Paint Technology Vol. 38, No. 496. May 1966.

solvent	∂	∂(SI)
n-Pentane	(7.0)	14.4
n-Hexane	7.24	14.9
Freon® TF	7.25	-
n-Heptane	(7.4)	15.3
Diethyl ether	7.62	15.4
1,1,1 Trichloroethane	8.57	15.8
n-Dodecane	-	16.0
White spirit	-	16.1
Turpentine	-	16.6
Cyclohexane	8.18	16.8
Amyl acetate	(8.5)	17.1
Carbon tetrachloride	8.65	18.0
Xylene	8.85	18.2

Ethyl acetate	9.10	18.2
Toluene	8.91	18.3
Tetrahydrofuran	9.52	18.5
Benzene	9.15	18.7
Chloroform	9.21	18.7
Trichloroethylene	9.28	18.7
Cellosolve® acetate	9.60	19.1
Methyl ethyl ketone	9.27	19.3
Acetone	9.77	19.7
Diacetone alcohol	10.18	20.0
Ethylene dichloride	9.76	20.2
Methylene chloride	9.93	20.2
Butyl Cellosolve®	10.24	20.2
Pyridine	10.61	21.7
Cellosolve®	11.88	21.9
Morpholine	10.52	22.1
Dimethylformamide	12.14	24.7
n-Propyl alcohol	11.97	24.9
Ethyl alcohol	12.92	26.2
Dimethyl sulphoxide	12.93	26.4

n-Butyl alcohol	11.30	28.7
Methyl alcohol	14.28	29.7
Propylene glycol	14.80	30.7
Ethylene glycol	16.30	34.9
Glycerol	21.10	36.2
Water	23.5	48.0

Also we should not forget about the SI conversion of solubility parameter:

$$\partial/\mathbf{MPa}^{½} = 2.0455 \times \partial\ /\mathrm{cal}^{½}\mathrm{cm}^{-3/2}$$

In 1966 Charles M. Hansen divided the total Hildebrand solubility parameters into three parts which are: a dispersion force component (δ_d), a hydrogen bonding component (δ_h), end a polar component (δ_p).

And the equation for it will be:

$$\delta_t{}^2 = \delta_d{}^2 + \delta_p{}^2 + \delta_h{}^2$$

It gives wider perspective and explains why polarity, and its effect on the solubility.

Table 4: *Hansen Parameters for Solvents at 25°C*

(values selected from Hansen's 1971 parameters listed in Handbook of Solubility Parameters, Allan F. M. Barton. Ph.D., CRC Press, 1983, page 153-157)

Solvent	∂/MPa ^{½}			
	∂_t	∂_d	∂_p	∂_h
Alkanes				
n-Butane	14.1	14.1	0.0	0.0
n-Pentane	14.5	14.5	0.0	0.0
n-Hexane	14.9	14.9	0.0	0.0
n-Heptane	15.3	15.3	0.0	0.0
n-Octane	15.5	15.5	0.0	0.0
Isooctane	14.3	14.3	0.0	0.0
n-Dodecane	16.0	16.0	0.0	0.0
Cyclohexane	16.8	16.8	0.0	0.2
Methylcyclohexane	16.0	16.0	0.0	0.0
Aromatic Hydrocarbons				
Benzene	18.6	18.4	0.0	2.0
Toluene	18.2	18.0	1.4	2.0
Napthalene	20.3	19.2	2.0	5.9
Styrene	19.0	18.6	1.0	4.1
o-Xylene	18.0	17.8	1.0	3.1
Ethyl benzene	17.8	17.8	0.6	1.4

p- Diethyl benzene	18.0	18.0	0.0	0.6
Halohydrocarbons				
Chloro methane	17.0	15.3	6.1	3.9
Methylene chloride	20.3	18.2	6.3	6.1
1,1 Dichloroethylene	18.8	17.0	6.8	4.5
Ethylene dichloride	20.9	19.0	7.4	4.1
Chloroform	19.0	17.8	3.1	5.7
1,1 Dichloroethane	18.5	16.6	8.2	0.4
Trichloroethylene	19.0	18.0	3.1	5.3
Carbon tetrachloride	17.8	17.8	0.0	0.6
Chlorobenzene	19.6	19.0	4.3	2.0
o-Dichlorobenzene	20.5	19.2	6.3	3.3
1,1,2 Trichlorotrifluoroethane	14.7	14.7	1.6	0.0
Ethers				
Tetrahydrofuran	19.4	16.8	5.7	8.0
1,4 Dioxane	20.5	19.0	1.8	7.4
Diethyl ether	15.8	14.5	2.9	5.1
Dibenzyl ether	19.3	17.4	3.7	7.4
Ketones				
Acetone	20.0	15.5	10.4	7.0
Methyl ethyl ketone	19.0	16.0	9.0	5.1
Cyclohexanone	19.6	17.8	6.3	5.1

Diethyl ketone	18.1	15.8	7.6	4.7
Acetophenone	21.8	19.6	8.6	3.7
Methyl isobutyl ketone	17.0	15.3	6.1	4.1
Methyl isoamyl ketone	17.4	16.0	5.7	4.1
Isophorone	19.9	16.6	8.2	7.4
Di-(isobutyl) ketone	16.9	16.0	3.7	4.1
Esters				
Ethylene carbonate	29.6	19.4	21.7	5.1
Methyl acetate	18.7	15.5	7.2	7.6
Ethyl formate	18.7	15.5	7.2	7.6
Propylene 1,2 carbonate	27.3	20.0	18.0	4.1
Ethyl acetate	18.1	15.8	5.3	7.2
Diethyl carbonate	17.9	16.6	3.1	6.1
Diethyl sulfate	22.8	15.8	14.7	7.2
n-Butyl acetate	17.4	15.8	3.7	6.3
Isobutyl acetate	16.8	15.1	3.7	6.3
2-Ethoxyethyl acetate	20.0	16.0	4.7	10.6
Isoamyl acetate	17.1	15.3	3.1	7.0
Isobutyl isobutyrate	16.5	15.1	2.9	5.9
Nitrogen Compounds				
Nitromethane	25.1	15.8	18.8	5.1
Nitroethane	22.7	16.0	15.5	4.5

2-Nitropropane	20.6	16.2	12.1	4.1
Nitrobenzene	22.2	20.0	8.6	4.1
Ethanolamine	31.5	17.2	15.6	21.3
Ethylene diem me	25.3	16.6	8.8	17.0
Pyridine	21.8	19.0	8.8	5.9
Morpholine	21.5	18.8	4.9	9.2
Analine	22.6	19.4	5.1	10
N-Methyl-2-pyrrolidone	22.9	18.0	12.3	7.2
Cyclohexylamine	18.9	17.4	3.1	6.6
Quinoline	22.0	19.4	7.0	7.6
Formamide	36.6	17.2	26.2	19.0
N,N-Dimethylformamide	24.8	17.4	13.7	11.3
Sulfur Compounds				
Carbon disulfide	20.5	20.5	0.0	0.6
Dimethylsulphoxide	26.7	18.4	16.4	10.2
Ethanethiol	18.6	15.8	6.6	7.2
Alcohols				
Methanol	29.6	15.1	12.3	22.3
Ethanol	26.5	15.8	8.8	19.4
Allyl alcohol	25.7	16.2	10.8	16.8
1-Propanol	24.5	16.0	6.8	17.4
2-Propanol	23.5	15.8	6.1	16.4

1-B utanol	23.1	16.0	5.7	15.8
2-Butanol	22.2	15.8	5.7	14.5
Isobutanol	22.7	15.1	5.7	16.0
Benzyl alcohol	23.8	18.4	6.3	13.7
Cyclohexanol	22.4	17.4	4.1	13.5
Diacetone alcohol	20.8	15.8	8.2	10.8
Ethylene glycol monoethyl ether	23.5	16.2	9.2	14.3
Diethylene glycol monomethyl ether	22.0	16.2	7.8	12.7
Diethylene glycol monoethyl ether	22.3	16.2	9.2	12.3
Ethylene glycol monobutyl ether	20.8	16.0	5.1	12.3
Diethylene glycol monobutyl ether	20.4	16.0	7.0	10.6
1 -Decanol	20.4	17.6	2.7	10.0
Acids				
Formic acid	24.9	14.3	11.9	16.6
Acetic acid	21.4	14.5	8.0	13.5
Benzoic acid	21.8	18.2	7.0	9.8
Oleic acid	15.6	14.3	3.1	14.3
Stearic acid	17.6	16.4	3.3	5.5
Phenols				
Phenol	24.1	18.0	5.9	14.9
Resorcinol	29.0	18.0	8.4	21.1
m-Cresol	22.7	18.0	5.1	12.9

Methyl salicylate	21.7	16.0	8.0	12.3
Polyhydric Alcohols				
Ethylene glycol	32.9	17.0	11.0	26.0
Glycerol	36.1	17.4	12.1	29.3
Propylene glycol	30.2	16.8	9.4	23.3
Diethylene glycol	29.9	16.2	14.7	20.5
Triethylene glycol	27.5	16.0	12.5	18.6
Dipropylene glycol	31.7	16.0	20.3	18.4
Water	47.8	15.6	16.0	42.3

As it was mentioned already carbon dioxide is non-polar molecule, and it can dissolve only non-polar molecules. Carbon dioxide is non polar but still have small value for other two parameters. It has strong dispersion solubility parameter which is simply almost total Hildebrand solubility parameter. It is shown on graph below.

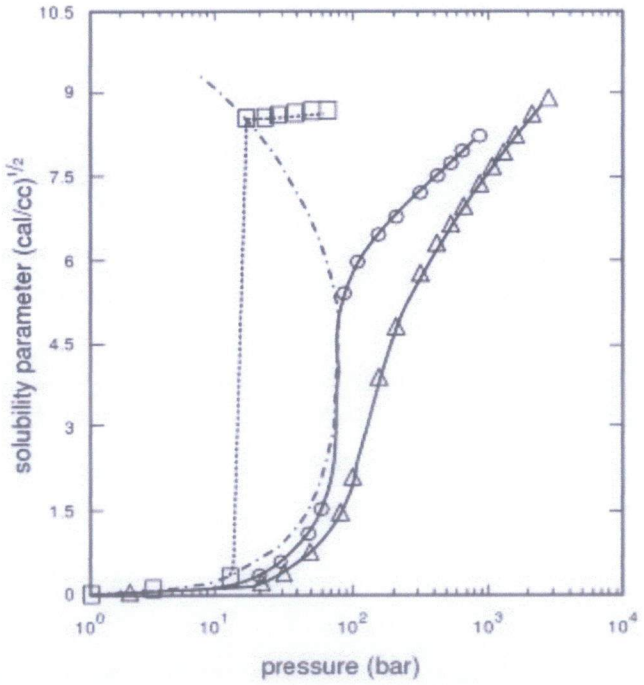


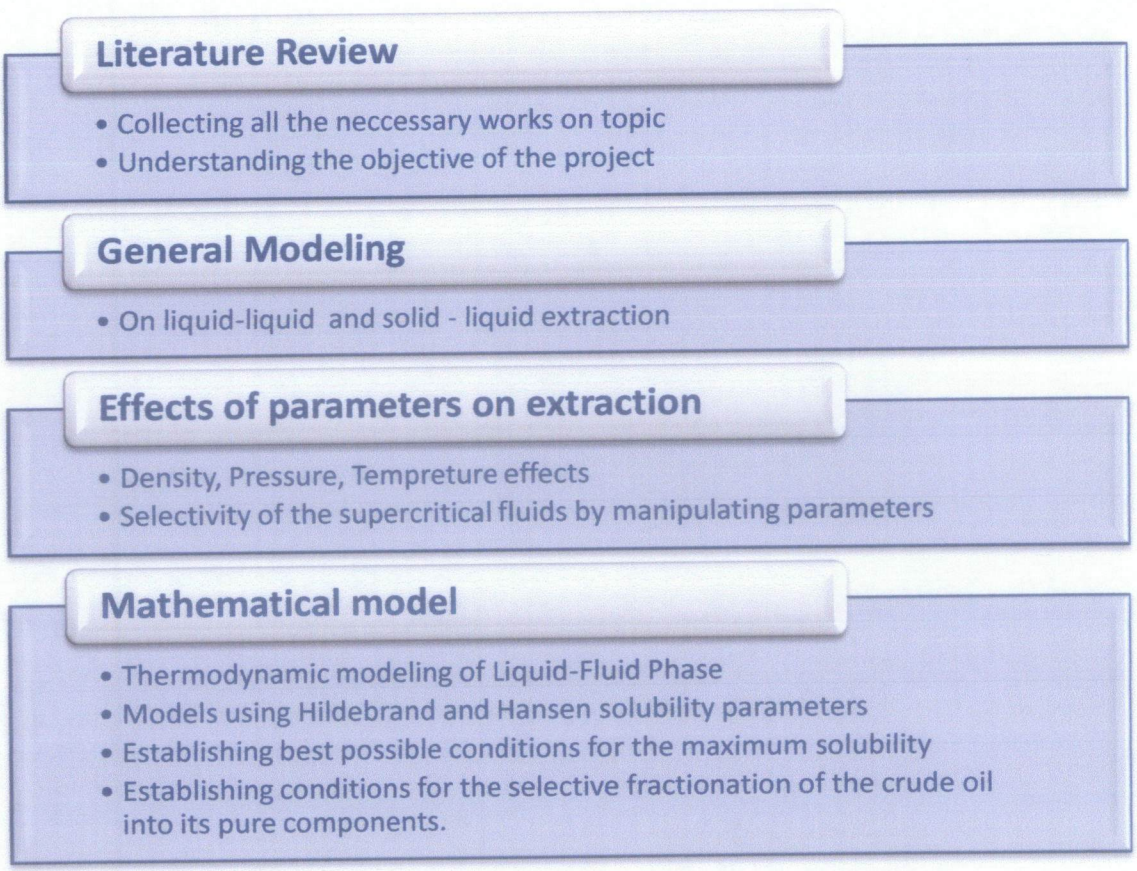
Figure 2: *Hildebrandt solubility parameters for CO2 (□) 30°C; (○) 31°C; (Δ)70°C*

In the graph above it is possible to see that the solubility parameter is changing with both pressure and temperature. And it should be noticed that when it is in the near critical point the dramatic change in solubility can be accomplished with just a little change in pressure. This shows us that it is possible to fractionate the crude oil into its components.

CHAPTER 3

METHODOLOGY

3.1 Research Methodology



3.2 Key Milestones

Table 5: Key Milestone for FYP 1

Event or Deliverable	Target Date
Submission of Extended Proposal	Week 6
Proposal Defense	Week 8 – 9
Submission of draft Interim Report	Week 13
Submission of Interim Report	Week 14

Table 6: Key Milestone for FYP 2

Event or Deliverable	Target Date
Submission of Progress Report	Week 8
Pre - SEDEX	Week 11
Submission of Draft Report	Week 12
Submission of Dissertation (Soft Bound)	Week 13
Submission of Technical Paper	Week 13
Oral Presentation	Week 14
Submission of Dissertation (Hard Bound)	Week 15

3.3 Gantt Chart

Table 7 Project Gantt chart

Timelines for FYP 2

No.	Detail/ Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
1	Project Work Continues																
2	Submission of Progress Report										11th Nov 2013						
3	Project Work Continues																
4	Pre-EDX												2th Dec 2013				
5	Submission of Draft Report										9th Dec						
6	Submission of Dissertation (soft bound)											16th Dec 2013					
7	Submission of Technical Paper											16th Dec 2013					
8	Oral Presentation												23th – 27th Dec 2013				
9	Submission of Project Dissertation (Hard Bound)												2nd Jan 2014				

Mid-Semester Break

Suggested milestone

Process

CHAPTER 4

RESULTS AND DISCUSSION

Crude oil is complex mixture of different hydrocarbons mostly. It consist in itself molecules of different sizes and shapes and properties. We can categorize crude oil as:

Table 8: *Composition of crude oil by weight*

Hydrocarbon	**Average**	**Range**
Paraffins	30%	15 to 60%
Naphthenes	49%	30 to 60%
Aromatics	15%	3 to 30%
Asphaltics	6%	remainder

But if to be more specific in terms of the chemical element composition we can say that crude oil consist of:

Table 9: *Element Percent range of Crude oil.*

Carbon	83 to 87%
Hydrogen	10 to 14%
Nitrogen	0.1 to 2%
Oxygen	0.05 to 1.5%
Sulfur	0.05 to 6.0%
Metals	< 0.1%

We have to pay attention not to the element because we deal with molecules and molecules completely behave different from the atom elements.

Paraffins which are also named Alkanes are saturated hydrocarbons and consist only of carbon and hydrogen atoms. Its general chemical formula is $\mathbf{C_nH_{2n+2}}$ e.g. a pentane (C_5H_{12}). All bonds are single bonds which form an open chain and do not form cyclic structure. From C_5 to C_{17} alkanes usually are liquid and above are solid. One of the most important things to mention is that paraffins are non-polar which means that carbon dioxide can dissolve them.

Naphthenes also known as the Cycloalkanes are cyclic structures and only consist of the carbon and hydrogen atoms. General formula is $\mathbf{C_nH_{2n}}$. It has same chemical properties as alkanes but the boiling point is quite higher. But again those are non polar molecules.

Aromatic hydrocarbons are consist of benzene rings with chemical formula $\mathbf{C_nH_n}$ it has double bonds and are unsaturated. As for the resonance structure it is non-polar molecule but since p orbitals of are large and polarizable, makes this class of molecules more polar than alkanes. Which means it will have larger solubility parameter.

Asphaltic molecules are can be really large molecules and that is why they can have different polarities, whether be polar or no- polar.

By using and manipulating the solubility parameters of the hydrocarbons we will able to fractionate the crude oil as almost like in distillation process.

Distillation process basically fractionates the crude oil according to boiling point temperatures. And the in table below it shows the fractionation components of crude oil in one distillation column.

Table 10: *Crude oil fractionation by distillation*

Name of component	**Fractionation Temperature range**	**Carbon number range**
Petroleum Gas	< 40°C	C_1-C_7
Gasoline	40°C - 200°C	C_5-C_{12}
Kerosene	175°C - 250°C	C_{12}-C_{16}
Diesel	250°C -350°C	C_{14}-C_{20}
Lubricating Oil	350°C >	C_{20}>

It is common to us that the solubility parameters increases with increasing of vaporization enthalpy which means larger molecules will have larger solubility parameters as it can be seen from the table above.

Since our criteria of fractionation should be as much as possible similar to the criteria of the distillation products then we should know mixture solubility parameter of the each fractionation component above.

The total Hildebrand solubility parameter of the mixture can be estimated by averaging the Hildebrand values of individual components.

For the gasoline components we can build the table accordingly:

Table 11: Major Components of Gasoline (Adapted from Air Force 1989)

Component	Percentage Composition	∂_d ∂/MPa ^{½}	∂_p ∂/MPa ^{½}	∂_h ∂/MPa ^{½}	∂_t ∂/MPa ^{½}
n-alkanes					
C_5	3.0	14.5	0	0	14.5
C_6	11.6	14.9	0	0	14.9
C_7	1.2	15.3	0	0	15.3
C_9	0.7	15.6*	0	0	15.6
C_{10}-C_{13}	0.8	15.7*-16.1*	0	0	15.7-16.1
Total n-alkane	17.3	14.9	0	0	14.9
Branched alkanes					
C_4	2.2	14.1	0	0	14.1
C_5	15.1	14.5	0	0	14.5
C_6	8.0	14.9	0	0	14.9
C_7	1.9	15.3	0	0	15.3
C_8	1.8	15.5	0	0	15.5
C_9	2.1	15.6*	0	0	15.6
C_{10}-C_{13}	1.0	15.7*-16.1*	0	0	15.7-16.1
Total of branched	32.0	14.8	0	0	14.8
Cycloalkanes					
C_6	3.0	16.8	0	0.2	16.8
C_7	1.4	16.9*	0	0.2	16.9
C_8	0.6	17*	0	0.2	17
Total cycloalkanes	5.0	16.9	0	0.2	16.9

Olefins					
C_6	1.8	18.4*	0.0	2.0	18.6
Total olefins	1.8	18.4	0	2.0	18.6
Aromatics					
benzene	3.2	18.4	0.0	2.0	18.6
Toluene	4.8	18.0	1.4	2.0	18.2
xylenes	6.6	17.8	1.0	3.1	17.8
ethybenzene	1.4	17.8	0.6	1.7	17.8
C_3 - benzenes	4.2	18.4*	0.0	2.0	18.6
C_4 - benzenes	7.6	18.4*	0.0	2.0	18.6
others	2.7				
Total aromatics	30.5	18.2	0.5	2.22	18.4
TOTAL AVERAGE		16.14			**16.29**

*(*are assumed values from similar chemical groups)*

We can see from the table that aromatics can have slight Hansen polar and hydrogen solubility parameters but those parameters are small and do not significantly change the total Hildebrand parameter. To dissolve polar molecules it is also possible by adding polar co-solvents such as methanol or ethanol.

The average value of total Hildebrand solubility value is **16.29 MPa** ^{½} and if we manage to get the solubility parameter to this exact value then we will have our best possible extraction.

For the gasoline to be soluble the supercritical carbon dioxide should have the same solubility parameter. That means that solubility parameter (δ) of the supercritical carbon dioxide should be **16.29 MPa** ^{½} which is equals to **8.145 cal^{½}cm$^{-3/2}$.**

By plugging in this value it into the equation derived by Giddings and co-workers (1968-1969):

$$\delta = 1.25 P_C^{\frac{1}{2}} (\rho_r / \rho_{r,1})$$

$P_c = critical\ pressure\ of\ the\ gas\ or\ liquid = 73.8\ bar$

$\rho_r = Reduced\ density\ of\ the\ gas\ or\ liquid = \frac{\rho}{\rho_c}$

$\rho_{r,1} = Reduced\ density\ of\ the\ gas\ or\ liquid\ at\ its\ normal\ boiling\ T \approx 2.66$

By taking a close look at the equation above it is possible to notice that the equation is related with density of the supercritical solvent. The table with data of the density with changing pressure and temperature (Gupta, Shim, 2007) is provided below:

Table 12: *Density of Carbon Dioxide*

P (bar)	T (°C)					
	32	***40***	***70***	***100***	***200***	***300***
70	5.491	4.4995	3.2606	2.7221	1.8955	1.5008
74	7.1573	5.0914	3.524	2.9136	2.0106	1.5582
75	8.3147	5.2609	3.592	2.9622	2.0395	1.61
76	12.668	5.4415	3.6608	3.0112	2.0684	1.6319
77	13.673	5.6348	3.7305	3.0604	2.0974	1.6537
78	14.183	5.8429	3.8011	3.11	2.1264	1.6756
79	14.539	6.0684	3.8726	3.1599	2.1554	1.6975
80	14.818	6.3144	3.9451	3.2101	2.1845	1.7194
90	16.277	11.032	4.7271	3.7302	2.4778	1.9387
100	16.912	14.283	5.6299	4.2846	2.7751	2.1585
200	20.012	19.082	14.975	10.919	5.8809	4.3604
300	21.37	20.675	17.904	15.039	8.8509	6.4671
360	21.966	21.343	18.921	16.458	10.387	7.635
400	22.311	21.724	19.466	17.944	11.293	8.3647
500	23.046	22.524	20.553	18.604	13.188	10.013
600	23.654	23.178	21.397	19.653	14.669	11.427
700	24.176	23.734	22.09	20.492	15.862	12.642
800	24.636	24.22	22.682	21.194	16.852	13.693

900	25.047	24.653	23.2	21.798	17.692	14.611
1000	25.42	25.044	23.661	22.331	18.421	15.424

The density (ρ) values are shown in unit of $\boldsymbol{mol/liter}$. The **critical point density** ($\boldsymbol{\rho_c}$) is $\boldsymbol{10.625\ mol/liter.}$

And using the equation of the Giddings and co-workers we can get the values for the solubility parameter (δ):

Table 13: *Solubility parameter of Carbon Dioxide*

P (bar)	SOLUBLITY PARAMETER ($cal^{½}cm^{-3/2}$)					
	32	***40***	***70***	***100***	***200***	***300***
70	2.086	1.71	1.239	1.034	0.72	0.57
74	2.719	1.934	1.339	1.107	0.764	0.592
75	3.159	1.978	1.365	1.125	0.775	0.612
76	4.813	2.068	1.391	1.144	0.786	0.62
77	5.195	2.141	1.417	1.163	0.797	0.628
78	5.389	2.22	1.444	1.182	0.808	0.637
79	5.524	2.306	1.471	1.201	0.819	0.645
80	5.63	2.399	1.499	1.22	0.83	0.653
90	6.184	4.192	1.796	1.417	0.941	0.737
100	6.426	5.427	2.139	1.628	1.054	0.82
200	7.604	7.25	5.69	4.149	2.234	1.657
300	8.12	7.855	6.803	5.714	3.363	2.458
360	8.346	8.109	7.189	6.253	3.947	2.901
400	8.477	8.254	7.396	6.818	4.292	3.179
500	8.756	8.558	7.809	7.069	5.011	3.804
600	8.987	8.807	8.13	7.467	5.574	4.342
700	9.186	9.018	8.393	7.786	6.027	4.803
800	9.364	9.202	8.618	8.053	6.403	5.203
900	9.517	9.367	8.815	8.282	6.722	5.551
1000	9.658	9.515	8.99	8.485	7	5.861

The unit of the solubility parameter (δ) is in $\boldsymbol{cal^{½}cm^{-3/2}}$. Since our solubility parameter value for the gasoline is $\boldsymbol{8.145\ cal^{½}cm^{-3/2}}$. Then the best possible miscibility is

achievable when the supercritical carbon dioxide has that specific value which in our case we will prefer least possible temperature and pressure. And according to the Table 13 it is at:

- $\boldsymbol{Temperature = 32\ °C \quad Pressure = 300\ bar}$

We also can calculate for any specific solubility parameter by using the equation. As for our case we get the $\boldsymbol{\rho_r = 2.018}$ from Giddings and co-workers equation, which mean that the density of the supercritical carbon dioxide, ρ will be:

$$\rho = \rho_r \times \rho_c = 2.018 \times 10.625 \frac{mol}{l} = \boldsymbol{21.437\ mol/l}$$

Since we were looking at the vicinity of the critical point I will be referring to the table 11 (Gupta, Shim, 2007) .

To calculate how much of solute was dissolved in the supercritical carbon dioxide we can use the Hildebrand regular solution theory t :

$$\ln x_2 = \frac{\Delta H_f}{R}\left(\frac{1}{T_f} - \frac{1}{T}\right) - \frac{V_2 \Phi_1^2 (\delta_2 - \delta_1)^2}{RT}$$

And maximum possible composition of the solute in solvent is when the solubility parameters of solute and solvents are equal to each other. But the down coming of this equation is that it is only true for the non-polar solute in non-polar solvent. And the thumb rule of the theory is that $\delta_2 - \delta_1 = \pm 1$ is the miscibility range of the solute and solvent. It is true only for the non-polar solvents and solutes. We know that overall the carbon dioxide is non-polar molecule but we also know that it has quadrapole moment which suggests it can dissolve polar molecules. And example can be given to that is methanol wich has solubility parameter equal to 14.5 $\mathbf{cal^{½}cm^{-3/2}}$ and it still dissolve in the supercritical carbon dioxide which has solubility parameter around 7 at standard conditions.

To resolve this issue we can use the Hansen solubility parameter which basically divides the total Hildebrand solubility parameters into three parts which are: a dispersion force component (δ_d), a hydrogen bonding component (δ_h), end a polar component (δ_p).

$$\delta_t{}^2 = \delta_d{}^2 + \delta_p{}^2 + \delta_h{}^2$$

And this will explain the polarity phenomena.

Also Charles Hansen made a three-dimensional model in order to plot solute solubilities. By doubling the dispersion parameter axis, an approximately spherical volume of solubility was established for a solute. This volume, being spherical, can be described in a simple way as shown in the figure: the coordinates at the center of the solubility sphere are located by means of three component parameters (∂d, ∂p, ∂h), and the radius of the sphere is indicated, called the interaction radius (R).

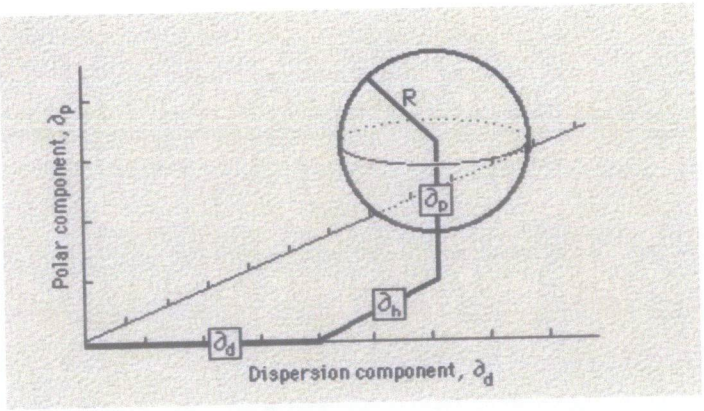


Figure 3: Hansen sphere model of solubility

A solute will be soluble s in a supercritical carbon dioxide (or any solvent) if the Hansen parameters for the solvent lie within the solubility sphere. The distance of the solvent (supercritical carbon dioxide) from the center of the solute solubility sphere is less than the radius of interaction for the polymer: The distance is given as:

$$D_{(S\text{-}P)} = [4(\partial_d s - \partial_d p)^2 + (\partial_p s - \partial_p p)^2 + (\partial_h s - \partial_h p)2]^{½}$$

where

$D_{(S-P)}$ = Distance between solvent and center of solubility sphere

$\partial_x s$=Hansen component parameter for solvent

$\partial_x p$=Hansen component parameter for solute

But we know that with pressure and temperature the Hansen solubility parameters change and in order to know the new values we use:

δ_d $\quad \frac{\delta_{dref}}{\delta_d} = \left(\frac{V_{ref}}{V}\right)^{-1.25}$

δ_p $\quad \frac{\delta_{pref}}{\delta_p} = \left(\frac{V_{ref}}{V}\right)^{-0.5}$

δ_h $\quad \frac{\delta_{href}}{\delta_h} = \exp[-1.32 \times 10^{-3}(T_{ref} - T) - \ln\left(\frac{V_{ref}}{V}\right)^{0.5}]$

Reference values are: δ_{dref}=15.6 $MPa^{1/2}$, δ_{pref}=5.2 $MPa^{1/2}$, δ_{href}=5.8 $MPa^{1/2}$, V_{ref}=39.13 cm^3/mole, T_{ref}=298.15 K

By using the above equation we can always predict the values for supercritical carbon dioxide.

Thus for every solubility parameter of supercritical carbon dioxide at different temperature and pressure we can develop the Hansen sphere model. Every compound which falls within this sphere will be soluble and thus enabling us to separate those components of crude oil. But for the sake of accuracy the sets of experimental data will be needed.

CHAPTER 5

CONCLUSION

Fractionation of the crude oil into components such as gasoline, kerosene, diesel and lubricating oil is possible. The main purpose of this project was to establish the best possible conditions for the best efficiency. And the method that was used in this paper was with solubility parameter by manipulating temperature and the pressure of the supercritical carbon dioxide. By manipulating those variables we will be changing the solubility parameter. The solubility parameter increases with increasing the size of the molecules in crude oil, for that reasons the increase of the solubility parameter in supercritical carbon dioxide is needed and that will be accomplished with increasing the pressure. But since the carbon dioxide is non-polar molecule it can dissolve only non-polar, but it can be overcome by adding co-solvents such as methanol or ethanol which will make it possible for the carbon dioxide to dissolve the polar molecules as well. As a conclusion it can be said that even through the distillation is dominating fractionation method for crude oil, it is our job to explore the possibility of the other alternative process.

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